MURI Interim Report (January 2009): Scientific Progress and accomplishments:

Nanoshells form the basic substrate for many of the surface enhanced spectroscopic studies undertaken under this MURI. We have developed a general facile technique to metallize dielectric nanoparticles. We hope this would widen the appeal of core-shell nanoparticles and simplify the production of larger quantities of core-shell nanoparticles. The SERS, and SERS – SEIRA techniques developed previously have been applied to elucidate reaction pathways in a metal catalyzed reaction, sensing small molecules that may not be bound to the nanoshell surface, and to determine the orientation of ds-DNA conjugated to nanoshells. Correlated single molecule SERS and electrical conductance measurements have been used to obtain the field strength in electromigrated junctions.

We have studied a variety of different structures as potential sensing substrates. Nanotori, nanorods dimers and nanoparticle-nanowire coupled systems were studied. Symmetry breaking and the evolution of the optical and field enhancement properties of nanoshells, nanoeggs, nanocups and a coupled ring-disk system were investigated. In the ring-disk coupled system when symmetry is broken, the plasmonic equivalent of electromagnetically induced transparency (EIT) - plasmonically induced transparency and its characteristic Fano resonance can be observed. This intriguing phenomenon may give rise to new highly sensitive LSPR sensing modalities.

1. We have developed an improved method for the growth of continuous Au shell layers on dielectric oxide nanoparticles. The reduction of Au3+ by CO(gas) results in the formation of thin, uniform shell layers on these nanoparticles at lower Au3+concentrations, where continuous shell layers are not achievable with current liquid phase reduction methods. This approach relies only on the introduction of CO(g) into the solution of prepared precursor nanoparticles and Au3+, and is not susceptible to variations in shell layer morphology influenced by preparation of reductant or precursor solutions, a limitation of current shell layer growth methods. The use of CO as a reductant also has the potential to transform the manufacturing of nanoshells from a batch to a continuous flow process. (Brinson, *et al.* “Nanoshells made easy: improving Au layer growth on nanoparticle surfaces”, Langmuir 24, 14166-14171 (2008)).
2. We report the direct observation, using surface-enhanced Raman and IR spectroscopies (SERS, SEIRA), of the insertion of ibuprofen molecules into hybrid lipid bilayers. The spectroscopic results combined from SERS and SEIRA studies provide chemical insight into the nature of ibuprofen-lipid interactions and have clinical importance in understanding the effects of NSAIDs on the integrity and permeability of the gastric mucosal membrane. The plasmonic nanostructures utilized in these studies are applicable for spectroscopic investigation of other biologically relevant phenomena in membrane mimics. This technique also provides a general method to investigate the SERS/SEIRA spectra of small molecules that may not be conveniently attached to a nanoshell substrate. (Levin, *et al.* “Surface Enhanced Raman and Infrared Spectroscopy (SERS and SEIRA) of Ibuprofen Intercalated Hybrid Bilayer Nanoshells”, Journal of Physical Chemistry B 112, 14168-14175 (2008)).

3. We have grown Pd islands on nanoshells to directly study the reaction pathways and intermediates formed during the catalytic hydrodechlorination of 1,1-dichloroethene in H_2O

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2009		**00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
MURI Interim Report (January 2009): Scientific Progress and accomplishments	**W911NF-04-1-0203**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Texas Tech University,Houston,TX**	8. PERFORMING ORGANIZATION REPORT NUMBER **; 46914-PH-MUR.95**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **U.S. Army Research Office, P.O. Box 12211, Research Triangle Park, NC, 27709-2211**	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **46914-PH-MUR.95**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**4**	

using surface-enhanced Raman spectroscopy (SERS). More broadly, the results highlight the exciting prospects of studying catalytic processes in water in situ, (Heck, et al. "Observing Metal-catalyzed Chemical Reactions in situ using Surface enhanced Raman Spectroscopy on Pd-Au Nanoshells, JACS 130, 16592-16600 (2008)).

4. Using previously developed techniques to improve the reproducibility of the SERS spectra of DNA, we have studied the orientation of ds-DNA attached to nanoshells. The relative change in orientation with packing density of the ds-DNA is also investigated. (Barhoumi, "Correlation of Molecular Orientation and Packing density in a dsDNA self-assembled monolayer observable with Surface Enhanced Raman Spectroscopy", JACS 130, 14040-1 (2008)).
5. We have investigated the fluorescence enhancement of ICG molecules as a function of distance from the surface of Au nanoshells (Au-NS). The distance between ICG molecules and the Au-NS surface is controlled by varying the thickness of silica shell spacer layers grown on the nanoshell surface. We observe a fluorescence enhancement of 50x when ICG molecules are spaced 7 nm from the Au nanoshell surface, which decreases with increasing distance of the molecule from the nanoshell surface.(Bardhan *et al.* "Nanoscale control of Near-Infrared Fluorescence Enhancement using Au Nanoshells", Small 4, 1716-1722 (2008)).
6. We report the formation of nanoshell-Jaggregate nanoparticle complexes that show coherent coupling between the localized plasmons of the metallic nanoparticle and the excitons of the molecular J-aggregate. The strength of this interaction is dependent on the specific plasmon mode of the nanoparticle coupled to the J-aggregate exciton. From a model based on Gans theory, we obtain an expression for the plasmon-exciton hybridized states of the complex. (Fofang, et al. "Plexcitonic Nanoparticles": Plasmon-exciton hybridization in a nanoshell-J-aggregate complex", Nano Letters 8, 3481-3487 (2008)).
7. Continuation of some recent research on simultaneous SERS and electrical conductance measurements from an electromigrated gaps, we demonstrates that simultaneous single-molecule SERS spectroscopy and conductance measurements of the currents due to optical rectification can provide a means of estimating the local electric field at the junction due to illumination.(Ward, *et al.* "Electronic and Optical Properties of Electromigrated Molecular Junctions", J. Phys.: Condensed Matter 20, 374118 (2008)).
8. We have used the finite element method (FEM) to examine the transition from gold–silica nanoshells to nanoeggs and nanocups. Both the near- and far-field effects of core offset and total particle size are considered, with an emphasis on spectral evolution and focused field enhancements. We conclude that, for a given pair of inner and outer shell radii, phase retardation and core offsets can be used together to design nanoparticles with a desired scattering and absorption ratio at the dipolar resonance. (Knight *et al.* "Nanoshells to nanoeggs to Nanocups: symmetry breaking beyond the quasistatic limit in complex plasmonic nanoparticles", New Journal of Physics 10, 105006 (2008)).
9. We have examined the effect of symmetry breaking in the concentric ring/disk cavity system. We consider both (a) displacement of the disk with respect to the center of the ring and (b) a ring of nonuniform thickness. In a concentric arrangement, the two major optically active

plasmon resonances are a subradiant bonding and a superradiant antibonding resonance formed by the interaction of the dipolar modes of the disk and the ring. For a nonconcentric alignment, the quadrupolar ring resonance interacts with the dipolar disk resonance and an asymmetric Fano resonance appears in the extinction spectrum that maybe exploited for LSPR sensing. (Hao,*et al.* "Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance", Nano Letters 8, 3983-3988 (2008)).

10. We have extended the plasmon hybridization method to nanorod dimers in symmetric and asymmetric situations. The nanorod dimer plasmons are formed from hybridization of the individual nanorod plasmon modes. The plasmonic interactions between the two nanorods depend strongly on the relative orientations of the particles. The largest electric field enhancements are induced for a nanorod dimer in a symmetric axial configuration. The magnitude of the field enhancements depend on the aspect ratio of the nanorods. Our approach can easily be applied to heterodimer situations in which two nanorods of arbitrary spatial orientation and size couple to an incident electromagnetic field. (Willingham, *et al.* "Plasmon hybridization in nanorod dimers", Appl. Phys. B 93, 209-216, (2008)).

11. We have investigated the plasmonic and optical properties of metallic tori using the plasmon hybridization (PH) method. We show that the plasmon resonances in a nanotorus results from hybridization of primitive plasmon modes that can be described as toroidal harmonics. The energies of the hybridized plasmon modes depend on the aspect ratio of the torus, which we define as the ratio of the radius of the tube r to the radius of the ring R, X= r/R. The plasmonic structure and optical absorption spectrum are found to be strongly dependent on the polarization. (Dutta, *et al.* "Plasmonic properties of a metallic torus" J. Chem. Phys. 129, 084706:1-9, (2008))

12. We have studied the polarization dependence of SERS in the coupled gold nanoparticle-nanowire system for nanoparticles of a variety of shapes. We find that the SERS spectra are strongly enhanced when the incident light is polarized across the junction between the particle and the wire and remarkably insensitive to the detailed geometrical structure of the nanoparticle. The measured Raman enhancements are in good agreement with theoretical simulations done using Finite Element Method (COMSOL). (Wei et al. "Polarization dependence of surface-enhanced Raman scattering in the gold nanoparticle-nanowire system", Nano Lett. 8, 2497-2502(2008)).

Complete List of Publications

1. Bruce Brinson, J. Britt Lassiter, Carly S. Levin, Rizia Bardhan, Nikolay Mirin and Naomi J. Halas, "Nanoshells made easy: improving Au layer growth on nanoparticle surfaces", Langmuir 24, 14166-14171 (2008).
2. Carly S. Levin, Janardan Kundu, Benjamin G. Janesko, Gustavo E. Scuseria, Robert Raphael, and Naomi J. Halas, "Surface Enhanced Raman and Infrared Spectroscopy (SERS and SEIRA) of Ibuprofen Intercalated Hybrid Bilayer Nanoshells", Journal of Physical Chemistry B 112, 14168-14175 (2008).

3. K. Heck, B. Janesko, G. Scuseria, M. S. Wong, and N. J. Halas, "Observing Metal-catalyzed Chemical Reactions *in situ* using Surface enhanced Raman Spectroscopy on Pd-Au Nanoshells, JACS 130, 16592-16600 (2008).
4. A. Barhoumi, D. Zhang, and N. J Halas, "Correlation of Molecular Orientation and Packing density in a dsDNA self-assembled monolayer observable with Surface Enhanced Raman Spectroscopy", JACS 130, 14040-1 (2008).
5. Rizia Bardhan, Nate K. Grady, and Naomi J. Halas, "Nanoscale control of Near-Infrared Fluorescence Enhancement using Au Nanoshells", Small 4, 1716-1722 (2008).
6. N. Fofang, Tae-Ho Park, P. Nordlander, and N. J. Halas, "Plexcitonic Nanoparticles": Plasmon-exciton hybridization in a nanoshell-J-aggregate complex", Nano Letters 8, 3481-3487 (2008).
7. D. R. Ward, G. D. Scott, Z. K. Keane, N. J. Halas, J. W. Ciszek, and D. Natelson, "Electronic and Optical Properties of Electromigrated Molecular Junctions", J. Phys.: Condensed Matter 20, 374118 (2008).
8. Mark Knight and N. J. Halas, "Nanoshells to nanoeggs to Nanocups: symmetry breaking beyond the quasistatic limit in complex plasmonic nanoparticles", New Journal of Physics 10, 105006 (2008).
9. F. Hao, S. Maier, N. J Halas, and P. J. Nordlander, "Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance", Nano Letters 8, 3983-3988 (2008).
10. Plasmon hybridization in nanorod dimers, B. Willingham, D.W. Brandl, and P. Nordlander, Appl. Phys. B 93(2008)209-216
11. Plasmonic properties of a metallic torus, C.M. Dutta, T.A. Ali, D. W. Brandl, T.-H. Park, and P. Nordlander, J. Chem. Phys. 129(2008)084706:1-9
12. Polarization dependence of surface-enhanced Raman scattering in the gold nanoparticle-nanowire system, H. Wei, F. Hao, Y. Huang, P. Nordlander, and H.X. Xu, Nano Lett. 8(2008)2497-2502.

Submitted

13. Rizia Bardhan, Oara Neumann, N, Mirin, H. Wang, and N. J. Halas, "Au nanorice assemble electrolytically into mesostars", ACS Nano, accepted DOI: 10.1021/nn800657t.
14. Dongmao Zhang, Hui Wang, Oara Neumann, Aoune Barhoumi, Michael Perham, Jeffrey Hartgerink, Pernilla Wittung-Stafshede and Naomi J.Halas, "Gold nanoparticles can induce the formation of protein-based aggregates at physiological pH", submitted.
15. Nikolay Mirin and N. J. Halas, "Au nanocups: oriented 3D nanoantennas", submitted.
16. R. Bardhan, N. K. Grady, J. Cole, A. Joshi and N. J. Halas, "Fluorescence Enhancement by Au nanostructures: nanorods and nanoshells", submitted.
17. Fano resonance in plasmonic nanoparticle aggregates, N. A. Mirin, K. Bao, and P. Nordlander, Submitted to J. Phys. Chem. C.
18. Optical properties of nanoparticle arrays for oblique excitation using the Multiple Unit Cell Method, F. Le and P. Nordlander, to appear in J. Comput. Theor. Nanosci.